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I.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

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Rumford Professor in Harvard University.

Presented June 24th, 1879.

I PROPOSE the term "complex inorganic acid" for a class of compounds which may be considered as formed by the union of two or more acids with elimination of water in such a manner as to form a whole which in its chemical relations behaves like an acid containing a single radical. Compounds of this character were observed at an early period in the history of chemistry, but their real nature was for a long time entirely unknown, and our positive knowledge of the subject dates from the discovery of the silico-tungstates by Marignac in 1861.[*] Berzelius had long before described and analyzed a compound which we should now write

$$3\,SiO_2 \,.\, 2\,V_2O_5 \,.\, 2\,P_2O_5 \,.\, 6\,H_2O,$$

the chemical relations of which are still to be studied.[†] He had also noticed the formation of peculiar yellow compounds when phosphoric or arsenic acids are digested with molybdic teroxide.[‡] These were again noticed and partially studied by Svanberg and Struve,[§] who employed a solution of ammonic molybdate as a test for the presence of phosphoric acid. Sonnenschein* appears to have first shown that phosphoric oxide was an essential constituent of the yellow compound formed. Finally Debray assigned to the ammonium salt the formula

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[*] Ann. de Chimie et de Physique, (4,) iii. 55.

[†] Lehrbuch der Chemie, iii. 1058.

[‡] Lehrbuch, iii. 1044.

[§] K. Sv. Vet. Handlingar, 1848, p. 1.

$$20\,MoO_3 \,.\, P_2O_5 \,.\, 3\,(MH_4)_2O + 3\,H_2O,$$

and separated the corresponding acid.

In a paper presented to the Association of German Naturalists and Physicians in August, 1872,† Scheibler described salts of two different phosphotungstic acids, and gave formulas for the acids themselves, as well as for a sodium salt belonging to a third series, all of which, however, he regarded as provisional. Since then nothing further has appeared upon the subject from Scheibler's pen, and I have consequently felt at liberty to include the phosphotungstates in my own work.

My investigation of the complex inorganic acids had advanced but little before I found it necessary to study the alkaline salts of tungstic acid with special care. This study has alone occupied a great deal of time, and has proved one of extraordinary difficulty, in spite of the previous labors of Laurent, Lotz, Scheibler, Zettnow, Marignac, and others. The difficulties in question are mainly these: —

1. The alkaline tungstates are numerous and unusually complex. Salts of essentially different formulas approach so closely in percentage composition, that the differences lie very near the unavoidable errors of analysis. Thus Scheibler maintains that the formula of a particular sodium salt is

$$7\,WO_3 \,.\, 3\,Na_2O + 16\,aq,$$

while, according to Marignac, the same salt must be represented by

$$12\,WO_3 \,.\, 5\,Na_2O + 28\,aq.$$

The analyses are hardly sufficiently close to decide the question upon purely analytical grounds.

2. Almost all the alkaline tungstates are efflorescent in a very marked degree.

3. The salts of one series agree so closely in chemical properties with those of the next, that distinctive tests are wanting, and analysis does not always suffice to distinguish two salts even when unmixed. Mixtures are naturally very hard to deal with.

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* Journal für Prakt. Chemie, liii. 342.

† Berichte der Deutschen Chem. Gesellschaft, v. 801.

4. Monoclinic and triclinic forms predominate very largely, but owing to rapid efflorescence it is very difficult to make good measurements of crystals. The resemblance between the forms of different compounds is frequently very close.

5. Many salts are decomposed by boiling, or even by hot, water, yielding two or more different salts in solution. These usually recombine in the act of crystallization or on cooling the solution, but the reactions of hot and cold solutions are often, as I shall show, very different.

In determining the tungstic oxide in these compounds, I have employed the method of Berzelius with mercurous nitrate almost exclusively, but I have modified the process slightly so as to gain materially in accuracy. To the hot solution of the tungstate mercurous nitrate is added until in small excess. Mercuric oxide, prepared by precipitating the chloride by sodic hydrate, is then added until the yellow mercurous tungstate takes a reddish hue which is persistent after boiling. If the solution is boiled before filtering it clears rapidly, and the precipitate becomes rather more compact. The filtration and washing are then very easy and expeditious. The precipitate must be ignited as long as it loses weight. By this process Dr. Gooch, my assistant, obtained results which in two successive analyses of the same preparation rarely differed by 0.1%. The water determinations were always made by simple ignition. They almost invariably agree within a few hundredths. In the greater number of cases the alkaline base was determined from the loss, as the results obtained in this manner are far more accurate than those yielded by the direct method. But in some doubtful salts the alkali was determined directly. Ammonia was always estimated by boiling the compound with an excess of sodic hydrate, collecting the ammonia in chlorhydric acid, and weighing it as chloride.

The only objection to the method of determining tungstic oxide above given is, that the precipitate of mercurous tungstate is rather voluminous, so that it is necessary to work with quantities of alkaline tungstate not much exceeding one gramme in weight. I endeavored to overcome this difficulty by omitting the mercuric oxide and evaporating the solution and precipitate, after the addition of mercurous nitrate, to perfect dryness in a water bath, continuing the heat until all the free nitric acid was expelled. This method gave results which corresponded very closely with those obtained by the use of mercuric oxide to neutralize the free nitric acid, and in consequence of the extremely compact form of the dry mercurous tungstate, permitted the employment of much larger quantities of salt for analysis. On the other hand, it presents another difficulty, arising from the fact that the dry mercurous tungstate adheres with excessive tenacity to the evaporating vessels, whether of glass, porcelain, or platinum, so that the first method is on the whole to be preferred.

The separation of tungstic oxide from other bases is best effected by fusing the salt with an excess of potassio-sodic carbonate and dissolving out the alkaline tungstates formed.

Normal sodic tungstate has long been known, and all the analyses concur in assigning to it the formula

$$WO_4Na_2 + 2\,aq.$$

It is now to be had from various German firms in a state of purity, and forms the most convenient material for the study of the compounds of tungsten. The acid salt analyzed by Anthon, and to which the formula

$$W_2O_7Na_2 + 4\,aq$$

was long ascribed, is now well known to have an entirely different composition; but Lefort* has recently endeavored to show that ditungstates and tritungstates really exist, and has described a number of salts of each series. Lefort obtains sodic ditungstate by adding glacial acetic acid to a saturated solution of the neutral salt until the reaction with litmus becomes acid. After a day or two the salt separates in long prismatic crystals, with the formula

$$W_2O_7Na_2 + 6\,aq.$$

I have repeatedly attempted to prepare the ditungstate by this process, but without success in any one instance, the resulting salts being, as I shall show further on, in all cases very different in composition. Lefort prepared sodic tritungstate by pouring a concentrated solution of the ditungstate into a boiling solution of glacial acetic acid. His analyses agree fairly well with his formulas, and I have adopted his results without question, in the belief that my own inability to reproduce them was due to the omission in his paper of some matter of detail which appeared insignificant, but which was really important.

Ten to Four Sodium Salt.—The salt to which I have given this name appears to have been first observed by Forcher,† who obtained it by passing a current of carbonic dioxide for some days through a solution of the normal tungstate. Forcher gives the formula

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* Ann. de Chimie et de Physique, (5,) ix. 93.

† Wiener Akad. Berichte, xliv. 2, 177.

$$5\,WO_3 . 2\,Na_2O + 12\,H_2O,$$

and suggests, though without adducing any evidence in support of his view, that it may be a double salt, with the formula

$$3\,WO_3 . Na_2O + 2\,WO_3 . Na_2O.$$

Marignac, who appears to have been unacquainted with Forcher's paper, soon afterward described the same salt as an accidental product, attributing to it the formula

$$5\,WO_3 . 2\,Na_2O + 11\,H_2O.$$

Finally, Lefort * obtained it by the action of acetic acid upon a solution of the normal tungstate, and, without citing the results of Forcher, also proposed the formula

$$5\,WO_3 . 2\,Na_2O + 11\,H_2O.$$

I have obtained the salt by the following process, which appears to be the most convenient. Normal sodic tungstate,

$$WO_3 . Na_2O + 2\,aq,$$

is to be dissolved in water, and acetic acid added, in small portions at a time, to the boiling solution, until the reaction becomes strongly acid. Alcohol then precipitates the 10:4 tungstate as a heavy oil, which soon becomes a solid mass. The solution on standing some days deposits colorless crystals, which are usually much twinned, and, according to Marignac, belong to the monoclinic system. They effloresce readily in dry air and are soluble, according to Forcher's determination, in 12.6 parts of water at 22° C. When heated they fuse to a yellow liquid, which on cooling gives a white crystalline mass nearly insoluble in cold water but dissolved by long boiling. I assign to the crystallized hydrate the formula

$$10\,WO_3 . 4\,Na_2O + 23\,H_2O, \quad \text{or} \quad 10\,WO_3 . 4\,Na_2O . 2H_2O + 21\,aq,$$

with which all the analyses agree very closely. Of the salt,

$$\text{I.}\begin{cases}1.4152 \text{ gr. lost } 0.1963 \text{ gr. by ignition} & = 13.88\%\\ 0.4095 \text{ gr. gave } 0.3194 \text{ gr. } WO_3 & = 77.99\%\end{cases}$$

$$\text{II.}\begin{cases}1.1182 \text{ gr. lost on ignition } 0.1558 \text{ gr. water} & = 13.94\%\\ 0.8950 \text{ gr. gave } 0.6968 \text{ gr. } WO_3 & = 77.85\%\end{cases}$$

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* Loc. cit.

III. $\begin{cases} \text{1.3594 gr. lost on ignition 0.1862 gr. water} = 13.70\% \\ \text{0.5340 gr. gave 0.4155 gr. } WO_3 = 77.80\% \end{cases}$

IV. $\begin{cases} \text{1.1660 gr. lost on ignition 0.1624 gr. water} = 13.93\% \\ \text{0.5981 gr. gave 0.4659 gr. } WO_3 = 77.89\% \end{cases}$

V. $\begin{cases} \text{1.3594 gr. lost on ignition 0.1862 gr. water} = 13.70\% \\ \text{0.5340 gr. gave 0.4155 gr. } WO_3 = 77.80\% \end{cases}$

The formula $10\,WO_3 \,.\, 4\,Na_2O + 23\,aq$ requires

		Calc'd.	1.	2.	3	4.	5.	Forcher.	Marignac.
$10\,WO_3$	2320	77.80	77.99	77.85	77.80	77.89	77.80	77.82	77.88
$4\,Na_2O$	248	8.32	8.13	8.21	8.50	8.18	8.50	8.16	8.39
$23\,H_2O$	414	13.88	13.88	13.94	13.70	13.93	13.70	13.88	13.53
	2982	100.00						99.86	99.80

The means of all these analyses may be compared with the three formulas above given.

	WO_3	Na_2O	H_2O
For the ratio 10 . 4 . 22	78.27	8.37	15.36
" " 10 . 4 . 24	77.63	8.16	14.21
" " 10 . 4 . 23	77.80	8.32	13.88
Means of new analyses,	77.86	8.30	13.83

The analyses therefore leave no reasonable doubt as to the true constitution of the salt. The solution of the 10 : 4 sodic tungstate has a distinct acid reaction, but it is very difficult to determine the limits of the basicity in this series, because no salts could be obtained having a number of molecules of fixed base higher than four. On the other hand, the white insoluble mass obtained by igniting the crystalline hydrate must have the formula

$$10\,WO_3 \,.\, 4\,Na_2O,$$

and I consider it a true pyro-salt. When boiled for some time with water, the pyro-salt dissolves and the original salt crystallizes from the solution. The case appears to be exactly analogous to that of sodic metatungstate, the insoluble

$$4\,WO_3 \,.\, Na_2O$$

of Scheibler and Marignac, giving the normal sodic metatungstate,

$$4\,WO_3 \,.\, Na_2O + 10\,aq,$$

when heated with water in a sealed tube. The reactions of the 10 : 4 salt with metallic solutions are extremely similar to those of the 12 : 5 salt,

$$12\,WO_3 \,.\, 5\,Na_2O + 28\,aq,$$

so that in fact it is difficult to distinguish between the two in any other way than by the habitus of the crystals and by analysis.

When the 10 : 4 salt is dissolved in water and a current of sulphydric acid gas passed into the solution to the point of saturation, the liquid becomes at first yellow, and finally orange red. On standing or evaporation, it deposits brown tungstic sulphide, WS_3, and the still faintly yellow mother liquor gives fine colorless triclinic crystals, which are separate and distinct, not twinned or aggregated in masses like the 10 : 4 salt. These crystals after recrystallization have the formula of the 12 : 5 salt presently to be described, namely,

$$12\,Wo_3 \,.\, 5\,Na_2O + 28\,aq,$$

as the following analyses show : —

1.6491 gr. gave	1.2760 gr. WO_3	= 77.38%
2.3696 gr. lost	0.3308 gr. water	= 13.96%
2.0037 gr. "	0.2790 gr. "	= 13.92%

		Calc'd.	Found.
$12\,WO_3$	2784	77.38	77.38
$5\,Na_2O$	330	8.61	8.68
$28\,H_2O$	504	14.01	13.92 13.96
	3618	100.00	

The formation of the 12 : 5 from the 10 : 4 salt is easily explained, as well as the separation of the tungstic sulphide, since we have

$$2\,(10\,WO_3 \,.\, 4\,Na_2O) + 5\,H_2S = 12\,WO_3 \,.\, 5\,Na_2O + 3\,WO_3 \,.\, Na_2O + 5\,WS_3 + 5\,H_2O.$$

A concentrated solution of the 10 : 4 sodium salt is resolved by boiling into the 12 : 5 salt and other compounds difficult to isolate in a state of purity. When a hot solution of potassic bromide or nitrate is added to a boiling solution of the 10 : 4 sodium salt, a white crystalline precipitate is speedily formed, which has the formula

$$12\,WO_3 \,.\, 5\,K_2O + 10\,aq.$$

But if a cold solution of a potassic salt is added to a cold solution of the 10 : 4 sodium salt, a white crystalline precipitate is formed, which has the formula

$$10\,WO_3 \,.\, 4\,K_2O + 9\,aq.$$

Twelve to Five Sodium Salt. — This is the salt to which Scheibler gives the formula

$$7\,WO_3 \,.\, 3\,Na_2O + 16\,aq,$$

and which Marignac writes

$$12\,WO_3 \,.\, 5\,Na_2O + 28\,aq.$$

According to Lotz, the salt contains fourteen atoms of water in place of sixteen as found by Scheibler. I have adopted the formula of Marignac, which agrees best with the analyses. In preparing this salt I have employed Scheibler's method, which consists in nearly neutralizing a boiling solution of the neutral tungstate, $WO_4Na_2 + 2$ aq, by chlorhydric acid. When the proper quantity of chlorhydric acid is added, the 12 : 5 salt is formed at once, and crystallizes from the solution in large colorless crystals, which, according to Scheibler, are monoclinic; according to Marignac, triclinic. If the proportion of chlorhydric acid is just sufficient to give an onion-red reaction with litmus, crystals are obtained, which are either a combination or a mixture of equal molecules of the 10 : 4 and 12 : 5 salts. These crystals are, according to Dr. Gooch, triclinic; their habitus resembles that of the 12 : 5 rather than that of the 10 : 4 salt. In this salt, in two different preparations carefully dried and pressed with woollen paper,

I.	1.2546 gr. gave	0.9725 gr. WO_3	= 77.51%
	1.2320 gr. "	0.9554 gr. "	= 77.55%
	1.4680 gr. lost	0.2035 gr. water	= 13.86%
	1.7511 gr. "	0.2431 gr. "	= 13.88%
II.	1.0842 gr. gave	0.8407 gr. WO_3	= 77.54%
	1.0908 gr. "	0.8450 gr. "	= 77.47%
	1.6919 gr. lost	0.2362 gr. water	= 13.96%
	1.5259 gr. "	0.2125 gr. "	= 13.93%

The analyses agree closely with the formula

$$12\,WO_3 \,.\, 5\,Na_2O + 10\,WO_3 \,.\, 4\,Na_2O + 51\,aq,$$

or,

$$22\,WO_3 \,.\, 9\,Na_2O + 51\,aq,$$

which requires

		Calc'd	Mean	Found.			
22 WO_3	5104	77.57	77.52	77.51	77.55	77.54	77.47
9 Na_2O	558	8.48	8.57	...	...	...	...
51 H_2O	918	13.95	13.91	13.86	13.88	13.96	13.93
	6580	100.00	100.00				

I have already stated, that in repeated trials I had not been able to obtain the sodic ditungstate described and analyzed by Lefort, though the process given by him was followed implicitly. In one experiment the crystals obtained gave on analysis results which correspond closely with the formula

$$12\,WO_3 \,.\, 5\,Na_2O + 28\,\text{aq.}$$

1.9868 gr. lost on ignition	0.2786 gr. water	= 14.02%
1.2870 gr. " "	0.1806 gr. "	= 14.01%
0.9365 gr. gave	0.7243 gr. WO_3	= 77.34%
1.3560 gr. "	1.0483 gr. "	= 77.31%

	Calc'd.	Found.	
$12\,WO_3$	77.38	77.34	77.31
$5\,Na_2O$	8.61	8.66	
$28\,H_2O$	14.01	14.02	14.01
	100.00		

In this experiment the normal tungstate was dissolved in cold water to a very strong solution, glacial acetic acid was added in excess, and the whole allowed to stand for twenty-four hours, when prismatic crystals separated. In a second experiment a concentrated solution of sodic tungstate was heated to the boiling point and ordinary acetic acid added in excess. Alcohol then threw down a pasty mass, which, after re-solution in water and crystallization, gave on analysis results which corresponded with the formula

$$22\,WO_3 \,.\, 9\,Na_2O + 51\,\text{aq.}$$

1.0861 gr. lost on ignition	0.1492 gr. water	= 13.74%
1.3830 gr. " "	0.1895 gr. "	= 13.70%
0.8884 gr. gave	0.6899 gr. WO_3	= 77.66%
1.2746 gr. "	0.9902 gr. "	= 77.69%

	Calc'd.	Found.	
$22\,WO_3$	77.57	77.67	77.69
$9\,Na_2O$	8.48	8.60	
$51\,H_2O$	13.95	13.70	13.74
	100.00		

The small differences between the calculated formula and the direct results of the analyses, in this instance, are exactly such as would be produced by the admixture of a small percentage of the 10 : 4 sodium salt, which, as I have shown above, is formed when a solution of neutral sodic tungstate is boiled for some time with an excess of acetic acid.

The general result of my own study of the action of acetic acid upon the neutral tungstate is, that we obtain the 12 : 5, the 22 : 9, or the 10 : 4 salt, according to the circumstances of the case, the constitution of the salt formed depending mainly upon the degree of concentration of the acid and upon the duration of its action. These results are in no way inconsistent with those of Lefort, and his analyses seem to leave no reasonable doubt that he obtained various salts to be classed as ditungstates and tritungstates.

Potassic Tungstates. — When a hot solution of the 10 : 4 sodium salt is mixed with a hot solution of potassic nitrate, a white precipitate shortly appears in small colorless crystalline scales, which may be recrystallized by projecting them in very small quantities at a time into boiling water. This method, which was first given by Scheibler, enables us to redissolve the salt in water without loss from the excessively violent succussions which occur on heating the salt with water in the usual manner. The salt requires a rather large quantity of water for solution, and crystallizes almost completely from the cold liquid. Of this salt in the first preparation, —

0.9888 gr. lost on ignition 0.0510 gr. water = 5.18%
0.6513 gr. “ “ 0.0358 gr. “ = 5.49%
1.1663 gr. “ “ 0.0610 gr. “ = 5.23%
1.1287 gr. “ “ 0.0596 gr. “ = 5.28%
1.0068 gr. gave 0.8173 gr. WO_3 = 81.21%

In a second preparation,—

1.4312 gr. lost on ignition 0.0751 gr. water = 5.25%
1.5846 gr. “ “ 0.0832 gr. “ = 5.25%
0.5786 gr. gave 0.4686 gr. WO_3 = 80.99%
0.4773 gr. “ 0.3875 gr. “ = 81.20%
1.8957 gr. “ 1.5370 gr. “ = 81.08%

These analyses lead to the formula

$$12\,WO_3 \,.\, 5\,K_2O + 10\,aq,$$

which requires :—

		Calc'd.	Mean.	Found.			
				1.	2.		
$12\,WO_3$	2784	81.02	81.12	81.21	80.99	81.20	81.08
$5\,K_2O$	472	13.73	13.62	. . .	. . .	. . .	. . .
$10\,H_2O$	180	5.25	5.26	5.29 *	5.25	5.25	. . .
	3436	100.00					

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* Mean of the four determinations of water in the first preparation.

Marignac gives eleven molecules of water. Scheibler gives the formula $7\,WO_3\,.\,3\,K_2O + 6$ aq, but his analyses agree better with that of Marignac.

When normal potassic tungstate, WO_4K_2, is evaporated to dryness with boric hydrate, and the soluble salts are washed out from the mass, a salt is obtained which after recrystallization has the formula

$$10\,WO_3\,.\,4\,K_2O + 9\text{ aq}.$$

The same salt is formed when cold solutions of potassic nitrate or bromide are added to cold solutions of the 10 : 4 sodium salts. It resembles the 12 : 5 potassium salt, already described, so closely, that it is difficult to distinguish between the two. This salt has not been described by other writers upon the subject. In preparation *a*, from the action of boric acid upon normal potassic tungstate,

0.4566 gr. gave 0.3714 gr. WO_3 = 81.34%
0.5915 gr. lost on ignition 0.0331 gr. water = 5.59%

In preparation *b*, from the action of acetic acid upon the normal potassium salt,

0.7418 gr. gave 0.6024 gr. WO_3 = 81.21%
1.1104 gr. lost on ignition 0.0610 gr. water = 5.49%
0.7060 gr. gave 0.5736 gr. WO_3 = 81.27%
1.0266 gr. lost on ignition 0.0556 gr. water = 5.42%

These analyses correspond best with the formula

$$10\,WO_3\,.\,4\,K_2O + 9\text{ aq}.$$

		Calc'd.	Mean.			
$10\,WO_3$	2320	81.13	81.27	81.34	81.2	81.27
$4\,K_2O$	377.6	13.20	13.23	13.07	13.30	13.31
$9\,H_2O$	162	5.67	5.50	5.59	5.49	5.42
	2859.6	100.00				

It is probable that the salt had lost a little water by efflorescence. When normal potassic tungstate is dissolved in boiling water, it is decomposed into free alkali and 12 : 5 acid tungstate. The decomposition may be represented by the equation,

$$12\,(WO_3\,.\,K_2O) + 7\,H_2O = 12\,WO_3\,.\,5\,K_2O + 14\,KHO.$$

In the acid salt formed in this manner,

0.7738 gr. lost on ignition 0.0414 gr. water = 5.35%
1.0385 gr. gave 0.8411 gr. WO_3 = 80.99%

The formula $12\,WO_3 \,.\, 5\,K_2O + 10\,aq$ requires 81.02% WO_3 and 5.25% H_2O.

Ammonic Tungstates.— When a solution of ammonic chloride is added to one of the 10 : 4 sodic tungstate, beautiful white talcose scales are thrown down, which are but slightly soluble in cold water. After washing, they may be dissolved in boiling water without evolution of ammonia and recrystallized. The analyses of this salt agree fairly well with the formula

$$10\,WO_3 \,.\, 4\,Na_2O + 4\,\{10\,WO_3 \,.\, 4\,(NH_4)_2O\} + 50\,aq,$$

as the following analyses show :—

I. { 0.5658 gr. gave 0.4851 gr. WO_3 = 85.74%
  0.5602 gr. lost on ignition 0.0690 gr. water and ammonia = 12.31%

II. { 0.3346 gr. lost 0.0427 gr. " " = 12.77%
  0.3849 gr. gave 0.3294 gr. WO_3 = 85.59%

		Calc'd.	Mean.	Found.	
$50\,WO_3$	11600	85.42	85.62	85.74	85.59
$4\,Na_2O$	248	1.83	1.79	1.94	1.64
$16\,(NH_4)_2O$	832	6.12	12.54	12.31	12.77
$50\,H_2O$	900	6.63			
	13580	100.00	99.95		

Analyses (I.) and (II.) are of different preparations of the same salt. When commercial ammonic tungstate (containing a little sodic oxide) is dissolved in ammonia, and acetic acid is added to the filtered liquid, a white slightly soluble salt is obtained which after recrystallization has the formula

$$12\,WO_3 \,.\, 5\,(NH_4)_2O + 6\,aq.$$

In this salt :

0.9293 gr. lost on ignition 0.1087 gr. = { 11.69% NH_3 and H_2O
  88.31% WO_3.

0.5366 gr. " " 0.0626 gr. = { 11.66% NH_3 and H_2O
  88.34% WO_3

0.6602 gr. gave 0.2039 gr. platinum = 8.15% $(NH_4)_2O$

1.1241 gr. " 0.3370 gr. " = 7.92% "

		Calc'd.	Mean.	Found.	
$12\,WO_3$	2784	88.32	88.32	88.34	88.31
$5\,(NH_4)_2O$	260	8.24	8.03	8.15	7.92
$6\,H_2O$	108	3.44	3.64	3.51	3.77
	3152	100.00	99.99		

Marignac found in this salt five molecules of water. Lotz and Scheibler gave it the formula

$$7\,WO_3 \,.\, 3\,(NH_4)_2O + 3\,H_2O.$$

Marignac has also described and analyzed an ammonium salt to which he gives the formula

$$5\,WO_3 \,.\, 2\,(NH_4)_2O + 5\,H_2O.$$

I should double this formula, and write it

$$10\,WO_3 \,.\, 4\,(NH_4)O + 10\,H_2O,$$

so that it would then belong to the series of 10 : 4 salts, the existence of which I have endeavored to establish. According to Marignac, it breaks up by solution in water into the 12 : 5 and 8 : 3 salts.

$$2\{10\,WO_3 \,.\, 4(NH_4)_2O\} = 12\,WO_3 \,.\, 5(NH_4)_2O + 8\,WO_3 \,.\, 3(NH_4)_2O.$$

Zinc Salts.—When a solution of zincous sulphate is added in small excess to a hot solution of the 10 : 4 sodic tungstate, no precipitate is produced at first, but after a few seconds beautiful aggregates of white needles make their appearance, and continue to be deposited for some time. They are almost perfectly insoluble in boiling water. For analysis they were washed with cold water and dried in pleno over sulphuric acid. The zinc salt is soluble both in an excess of zincous sulphate and of sodic tungstate; hence the precipitate which is at first formed is instantly redissolved and does not become permanent until a small excess of the sulphate is added. In this salt,

0.3342 gr. lost on ignition	0.0349 gr. water	= 10.44%
0.6392 gr. gave	0.5128 gr. WO_8	= 80.50%
1.0205 gr. "	0.8200 gr. "	= 80.35%

These analyses correspond with the formula

$$6\,WO_3 \,.\, 2\,ZnO + 10\,aq.$$

		Calc'd.	Found.	
6 WO_8	1392	80.27	80.50	80.35
2 ZnO	162	9.34	9.14 (loss)	
10 H_2O	180	10.39	10.44	
	1734	100.00		

From this it appears that the zinc salt is formed by the decomposition of the 10 : 4 sodic tungstate. The result may be expressed by the equation,

$$10\,WO_3 \,.\, 4\,Na_2O + 4\,SO_4Zn = 6\,WO_3 \,.\, 2\,ZnO + 2\{2\,WO_3 \,.\, ZnO\} + 4\,SO_4Na_2.$$

The zincous ditungstate, as Lefort has shown, is readily soluble in water and remains in solution.

When a cold solution of zincous sulphate is added to a cold solution of the 10 : 4 sodium salt, a different result is obtained. A white precipitate is at first formed as before, which instantly redissolves. After a small excess of the sulphate has been added, the solution gives in a short time colorless needles of a second zinc salt. Like the 6 : 2 salt first described, this is insoluble in water, cold or hot, but readily dissolves in an excess of the tungstate or sulphate. When a large excess of the sulphate is present, the zincous tungstate does not separate from the solution. Of this salt in one preparation, dried over SO_4H_2:

0.6586 gr. lost on ignition 0.0706 gr. water = 10.72%

$$0.5894 \text{ gr. gave } \begin{cases} 0.0638 \text{ gr. } ZnO & = 10.82\% \\ 0.4606 \text{ gr. } WO_3 & = 78.16\% \end{cases}$$

These analyses lead to the formula

$$10\,WO_3 \,.\, 4\,ZnO + 18\,aq,$$

which requires

		Calc'd.	Found.
$10\,WO_3$	2320	78.16	78.16
$4\,ZnO$	324	10.92	10.82
$18\,H_2O$	324	10.92	10.72
	2968	100.00	99.70

In a second preparation of the same salt, dried by woollen paper,

1.0006 gr. gave by ignition 0.1663 gr. water, also 0.7322 gr. WO_3 and 0.1048 gr. ZnO = 16.62% water, 73.18% WO_3, and 10.47% ZnO.

These results correspond to the formula

$$10\,WO_3 \,.\, 4\,ZnO + 29\,aq,$$

which requires

		Calc'd.	Found.
$10\,WO_3$	2320	73.27	73.18
$4\,ZnO$	324	10.24	10.47
$29\,H_2O$	522	16.49	16.62
	3166	100.00	100.27

When a cold solution of zincous sulphate is added to a cold solution of the 22-atom sodium salt a precipitate is formed, which redissolves precisely as in the last-mentioned cases. After the solution of zinc has been added in small excess, white needles separate, which are insoluble in water, and have the formula

$$22\,WO_3 \,.\, 9\,ZnO + 66\,aq,$$

as the following analyses show:

1.4620 gr. gave 0.2509 gr. water on ignition, 1.0602 gr. WO_3 and 0.1508 gr. ZnO = 17.16% water, 72.52% WO_3, and 10.31% ZnO.

		Calc'd.	Found.
$22\,WO_3$	5104	72.69	72.52
$9\,ZnO$	729	10.38	10.31
$66\,H_2O$	1188	16.93	17.16
	7021	100.00	99.99

The salt was dried for some time upon woollen paper.

General Conclusions.—From my own investigations, as well as from those of other chemists who have preceded me, I arrive at the following classification of the alkaline tungstates as most nearly representing the present state of our knowledge. There are three series of salts, which may be termed respectively normal tungstates, meta-tungstates, and pyro-tungstates. The two first-named series may be represented by the following as typical salts: —

Normal Series.

$WO_3 \,.\, Na_2O + 2\,aq$	
$2\,WO_3 \,.\, Na_2O + 6\,aq$	Lefort.
$3\,WO_3 \,.\, Na_2O + 4\,aq$	"

Meta-Tungstates.

$4\,WO_3 \,.\, Na_2O + 10\,aq$	or	$W_4O_{11}(NaO)_2 + 10\,aq$	Scheibler
$6\,WO_3 \,.\, 2\,BaO + 12\,aq$	"	$W_6O_{16}(BaO_2)_2 + 12\,aq$	"
$8\,WO_3 \,.\, 3\,(NH_4)_2O + 8\,aq$	"	$W_8O_{21}(NH_4O)_6 + 8\,aq$	Marignac.
$10\,WO_3 \,.\, 4\,Na_2O + 23\,aq$	"	$W_{10}O_{26}(NaO)_8 + 23\,aq$	
$12\,WO_3 \,.\, 5\,Na_2O + 28\,aq$	"	$W_{12}O_{31}(NaO)_{10} + 28\,aq$	Marignac.
$14\,WO_3 \,.\, 6\,Na_2O + 42\,aq$	"	$W_{14}O_{36}(NaO)_{12} + 42\,aq$	"

The salts of the normal series require no special notice. As already stated, I have not succeeded in preparing the di- and tri-salts of Lefort, but there seems to be no reason to doubt their existence. The pyro-salts are obtained from the meta-salts by ignition, as insoluble crystalline masses, which are decomposed by long boiling with water. All the meta-tungstates with an alkaline base, appear to contain water of constitution and to have an acid reaction, but it is difficult to determine the quantity of basic hydrogen with certainty, and the mere fact that the salts have an acid reaction is not in itself conclusive evidence that they are in the strict chemical sense *acid.* Tungstates have been described by different chemists, which do not fall within either of the groups given above. In all these cases, however, it will be found on examination, that the analyses do not agree well with the formulas assigned, and that there is reason to believe that the salts studied were mixtures. I consider it at least probable that the tri-salts of Lefort belong in reality to the meta-series, their molecular weights being doubled. But it is of course possible that we have here cases of isomerism, and I much regret that I did not succeed in obtaining these salts for study and comparison. With respect to the double salt which I have described above, and which has the formula

$$12\,WO_3 \,.\, 5\,Na_2O + 10\,WO_8 \,.\, 4\,Na_2O + 51\,aq,$$

I may remark that it is possible that the compound is really

$$22\,WO_3 \,.\, 9\,Na_2O + 51\,aq,$$

and that it is not a double salt, but one term in a series which we obtain by again doubling the formulas of the meta-tungstates as I have given them above. The question is one which I must leave undecided for the present at least.

The analogy between the compounds of tungsten and molybdenum is in general so great, that we ought to expect to find alkaline molybdates corresponding to the three series of tungstates. We owe to Ullik the most complete examination of the molybdates which has been published. A careful study of his results will show that, while we have a number of molybdates to which there are apparently no corresponding tungstates, we have at least reason to believe in the existence of the three series of normal, meta, and pyro salts. Thus the following salts may be assumed as typical: —

Normal Series.

$MoO_3 \,.\, Na_2O + 2\,aq$
$2\,MoO_3 \,.\, Na_2O$ and with $1 \,.\, H_2O$

Meta Series.

$4\,MoO_3 \,.\, Na_2O + 6\,aq$ or $Mo_4O_{11}(NaO)_2 + 6\,aq$
$6\,MoO_8 \,.\, 2\,Na_2O + 14\,aq$ " $Mo_6O_{16}(NaO)_4 + 14\,aq$
$8\,MoO_3 \,.\, Na_2O \,.\, 2\,H_2O + 2\,aq$ " $Mo_8O_{21}(NaO)_2(HO)_4 + 2\,aq$

$10\,MoO_3 \,.\, Na_2O \,.\, 3\,H_2O + 9\,aq$ or $Mo_{10}O_{26}(NaO)_2(HO)_6 + 9\,aq$
$14\,MoO_3 \,.\, 6\,Na_2O + 44\,aq$ " $Mo_{14}O_{36}(NaO)_{12} + 44\,aq$
$16\,MoO_3 \,.\, 2\,Na_2O \,.\, 5\,H_2O + 3\,aq$ " $Mo_{16}O_{41}(NaO)_4(HO)_{10} + 3\,aq$
$18\,MoO_3 \,.\, 2\,BaO \,.\, 6\,H_2O + 2\,aq$ " $Mo_{18}O_{46}(BaO_2)_2(HO)_{12} + 2\,aq$

It may of course be maintained that the arrangement of the acid salts of molybdic oxide which I have adopted is purely arbitrary, and that they might be written with equal or greater probability in the usual manner, as members of the normal series, which would then be:

$MoO_3 \,.\, Na_2O + 2\,aq$
$2\,MoO_3 \,.\, Na_2O + aq$
$3\,MoO_3 \,.\, Na_2O + 7\,aq$
$4\,MoO_3 \,.\, Na_2O + 6\,aq$
$8\,MoO_3 \,.\, Na_2O + 2\,aq$
$9\,MoO_3 \,.\, BaO + 4\,aq$
$10\,MoO_3 \,.\, Na_2O + 12\,aq$
$16\,MoO_3 \,.\, Na_2O + 9\,aq.$

To this I reply that one arrangement is no more arbitrary than the other, since we have no positive knowledge of the constitution of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown. The commonly received view is therefore also a pure assumption. In any case, however, we have the two salts, represented respectively by the formulas

$4\,MoO_3 \,.\, Na_2O + 6\,aq$ or $Mo_4O_{11}(NaO)_2 + 6\,aq$
$14\,MoO_3 \,.\, 6\,Na_2O + 44\,aq$ " $Mo_{14}O_{36}(NaO)_{12} + 44\,aq,$

forming the upper and lower limits of a molybdic series corresponding to alkaline tungstates, and from these we may fairly infer the existence of the intermediate compounds. But one acid tungstate of the meta series is at present known, the salt

$$8\,WO_3 \,.\, Na_2O + 12\,aq, \quad \text{or} \quad W_8O_{23}(NaO)_2 + 12\,aq.$$

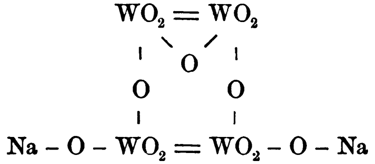
This may be considered as an acid salt of the 8-atom term, and written

$$8\,WO_3 \,.\, Na_2O \,.\, 2\,H_2O + 10\,aq,$$

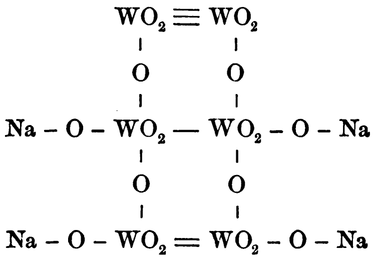
so that it will correspond to the molybdic salt

$$8\,MoO_3 \,.\, Na_2O \,.\, 2\,H_2O + 2\,aq.$$

But the supposition that acid metatungstates of the 4 : 1 series really exist, is in no way inconsistent with the view of the whole subject which I have taken. So far as I know, no attempt has been made to exhibit the mode of union of the elements in the higher tungstates. Our views of the subject will differ according as we consider tungsten as tetratomic or hexatomic. In what follows I have adopted the latter hypothesis, partly because the hexatomic character of tungsten is well marked in various compounds, as for example in WCl_6, and partly because the graphical representations are, on the whole, simpler. Moreover, if we consider tungsten to be tetratomic in the normal series, we obtain a reason for the existence and peculiar character of the meta series, by supposing that in this the metal is hexatomic. We may, to begin with, represent sodic metatungstate, $4\ WO_3 \,.\, Na_2O$, as follows:

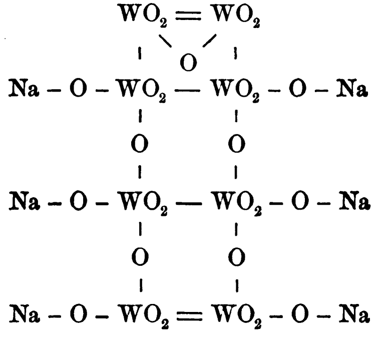


The next term in the series, $6\ WO_3 \,.\, 2\ Na_2O$, will then be

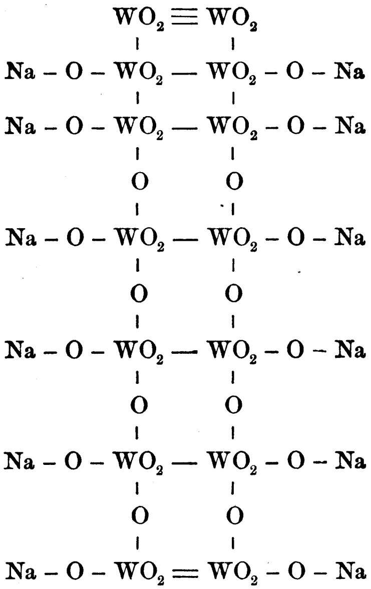


$$\begin{array}{rcccl} & WO_2 & \equiv & WO_2 & \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ Na - O - & WO_2 & - & WO_2 & - O - Na \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ Na - O - & WO_2 & = & WO_2 & - O - Na \end{array}$$

The third term, $8\ WO_3 \,.\, 3\ Na_2O$, may be represented by the graphical formula

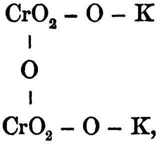


and so on for the other known terms, the highest, $14\ WO_3 \,.\, 6\ Na_2O$, being represented by the expression



$$\begin{array}{ccccc}
 & \mathrm{WO_2} & \equiv & \mathrm{WO_2} & \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & — & \mathrm{WO_2} & \mathrm{- O - Na} \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & — & \mathrm{WO_2} & \mathrm{- O - Na} \\
 & | & & | & \\
 & \mathrm{O} & & \mathrm{O} & \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & — & \mathrm{WO_2} & \mathrm{- O - Na} \\
 & | & & | & \\
 & \mathrm{O} & & \mathrm{O} & \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & — & \mathrm{WO_2} & \mathrm{- O - Na} \\
 & | & & | & \\
 & \mathrm{O} & & \mathrm{O} & \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & — & \mathrm{WO_2} & \mathrm{- O - Na} \\
 & | & & | & \\
 & \mathrm{O} & & \mathrm{O} & \\
 & | & & | & \\
\mathrm{Na - O -} & \mathrm{WO_2} & = & \mathrm{WO_2} & \mathrm{- O - Na}
\end{array}$$

It will be seen that, with this view of the subject, those terms in the series in which the number of atoms of sodic oxide is even are represented by formulas in which the free atoms of WO_2 are united, in part directly, and in part by oxygen, while the union is direct when the number of atoms of sodic oxide is odd. I shall return to this subject in speaking of the phosphotungstates and other complex inorganic acids. No great value can, in the present state of our knowledge, be attributed to formulas like the above. They afford, however, some assistance in showing the possible mode of formation of the different terms of the series, but various other constructions may be devised which are perhaps equally probable. In adopting provisionally the particular construction which I have used, I have simply followed the clew given by the commonly received formula for potassic dichromate,

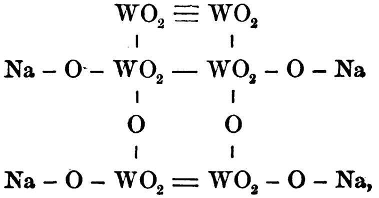


$$\begin{array}{l}
\mathrm{CrO_2 - O - K} \\
\;\;| \\
\;\;\mathrm{O} \\
\;\;| \\
\mathrm{CrO_2 - O - K,}
\end{array}$$

which of course gives a similar expression for the homologizing term in the acid tungstate series. So far as I am aware, no attempt has been made to formulate the remarkable compounds of tungsten described by Wöhler and others, and which may be expressed empirically by the formulas

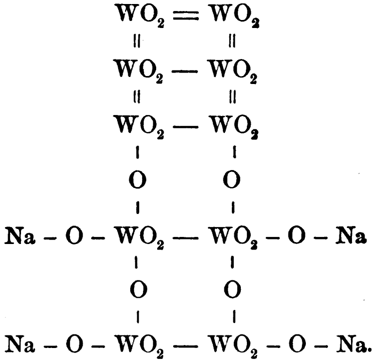
$$W_3O_9Na_2, \text{ and } W_5O_{14}Na_2.$$

If we double these formulas, we may bring them into harmony with the series of acid tungstates by writing them respectively,



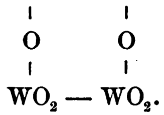
$$\begin{array}{ccccc} & WO_2 & \equiv & WO_2 & \\ & | & & | & \\ Na-O- & WO_2 & — & WO_2 & -O-Na \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ Na-O- & WO_2 & = & WO_2 & -O-Na, \end{array}$$

and



$$\begin{array}{ccccc} & WO_2 & = & WO_2 & \\ & \| & & \| & \\ & WO_2 & — & WO_2 & \\ & \| & & \| & \\ & WO_2 & — & WO_2 & \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ Na-O- & WO_2 & — & WO_2 & -O-Na \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ Na-O- & WO_2 & — & WO_2 & -O-Na. \end{array}$$

These formulas, if like the others purely hypothetical, have at least the merit of explaining the production of the insoluble sodium salts in a simple and natural manner. They are also entirely consistent with the simplest view which we can adopt with respect to the constitution of the blue oxide of tungsten, which is commonly written W_2O_5, but which is much more probably W_4O_{10}, and structurally

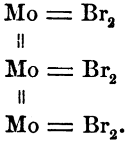


$$\begin{array}{ccc} WO_2 & — & WO_2 \\ | & & | \\ O & & O \\ | & & | \\ WO_2 & — & WO_2. \end{array}$$

The progress of science tends to show that the constitution of inorganic compounds is more complex than would at first appear. It would not be difficult to multiply instances which support this view, but I shall content myself with citing a single case, which has not been discussed, and which, strangely enough, has attracted but little attention. I refer to the remarkable series of compounds of molybdenum studied by Blomstrand* and by Atterberg.† Representative terms in this series are expressed by the formulas

$$\begin{array}{lll} Mo_3Cl_4 . Cl_2 & Mo_3Cl_4 . (OH)_2 & Mo_3Cl_4 . Br_2 \\ Mo_3Br_4 . Br_2 & Mo_3Br_4 . (OH)_2 & Mo_3Br_4 . SO_4 \end{array}$$

omitting water of crystallization for greater brevity. The action of alkalies upon the bromide $Mo_3Br_4 . Br_2$ produces first $Mo_3Br_4 . (OH)_2$, and afterward $Mo_3(OH)_4(OH)_2$, or $Mo_3(OH)_6$, the hydrate of the protoxide of molybdenum, usually written $MoO . OH_2$, or $Mo(OH)_2$. There is therefore good reason to believe that the lowest expression for this hydrate is $Mo_3(OH)_6$, the structural formula of the corresponding bromide being, perhaps,



$$\begin{array}{c} Mo = Br_2 \\ \| \\ Mo = Br_2 \\ \| \\ Mo = Br_2. \end{array}$$

In this formula the end atoms of molybdenum are tetratomic, and the middle atom hexatomic, which will perhaps explain the fact that there are but two movable atoms of bromine in a whole series of salts. If molybdic protoxide is Mo_3O_3, it is probable that the teroxide is not MoO_3, but rather some higher multiple of this expression, and we may extend the inference to WO_3 also.

With these preliminaries, I pass to the special subject of my work.

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* Journal für prakt. Chemie, lxxxii. 436.

† Några bidrag till Kännedomen om Molybden, Stockholm, 1872, p. 16.

(*To be continued.*)